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④ Bipolar membranes.

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<p>⑩ Priority: 23.11.83 US 554792 ⑯ Date of publication of application: 05.06.85 Bulletin 85/23 ⑯ Publication of the grant of the patent: 04.09.91 Bulletin 91/36 ⑯ Designated Contracting States: AT BE CH DE FR GB IT LI LU NL SE ⑯ References cited: GB-A- 1 038 777 US-A- 4 024 043</p>	<p>⑦ Proprietor: Chinese Petroleum Corporation 83 Chung Hwa Road Taipei Taiwan(TW) ⑦ Inventor: Liu, Kang-Jen 621 Strawbridge Street Bridgewater, Somerset, NJ 08807(US) Inventor: Lee, Ho-Lun 156 Livingstone Avenue New Providence, Union, NJ 07974(US) ⑦ Representative: Geldard, David Guthrie et al URQUHART-DYKES AND LORD Tower House Merrion Way Leeds West Yorkshire LS2 8PA(GB)</p>
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Description

Bipolar membranes are known to be useful for their ability to rectify alternating current, to improve desalination processes, to act as biological membranes, and to produce acids and bases from salts. This 5 latter property has great potential usefulness, since it allows the production of commercially important acids and bases from readily available neutral salts, e.g., the formation of HCl and NaOH from table salt. The potential for carrying out this type of conversion by means of bipolar membranes, a process known as 10 electrodialytic water-splitting, has not yet become an industrial process, primarily because of deficiencies in the properties of the bipolar membranes themselves and the difficulty of fabricating bipolar membranes 15 having reproducible properties on a large scale.

Many bipolar membranes prepared by various procedures have been reported in the literature. Initially, 20 bipolar membranes were prepared by bonding together polymer layers containing ion-exchange resin particles of opposite charges, as described for example in U.S. Patent 2,829,095. The fusion of conventional anion and cation transfer membranes (described for example in U.S. Patents 2,731,411 and 2,860,097) by 25 heat and pressure to yield bipolar membranes was also reported, as in U.S. Patent 3,372,101 and British Patent 1,038,777. Preparation of bipolar membranes from a single sheet of polymeric material by selective functionalization of one side to give anion or cation permeability and the other side permeability to ions of the opposite charge was described in U.S. Patents 3,388,080 and 3,654,125, as well as later U.S. Patents 4,024,043, 4,057,481 and 4,140,815. Although the bipolar membranes prepared by these later methods 30 have the desired properties of

- (i) Good mechanical strength,
- (ii) High permselectivity,
- (iii) Low membrane voltages,
- (iv) Stability, and

25 (v) Operability at high current density,

quality control is poor, particularly on a large scale, primarily due to the difficulty in controlling the diffusion into and reaction of reagents with the film. While such diffusion and reaction control is possible with small, 30 carefully selected uniform film, the non-uniformity inherent in large films and the strict requirements for diffusion and reaction control make large-scale manufacturing of the membranes quite difficult.

Another approach to making high-performance bipolar membranes with the desired properties listed 35 above may be found in US Patent 4116889. Unfortunately fabrication of such membranes has proven difficult because the formation of a uniform, fault-free, anion permeable layer by solution casting of a polymer system which is undergoing gelation requires careful control of the physical properties of the polymer, the mixing conditions, the casting process, and the gelation and drying times. Deviations from 40 these controls may lead to permanent scratches by the casting knife, non-uniform thickness and composition of the layer, and cracking. Accordingly, the fabrication of bipolar membranes which depends on the control of the formation of homogeneous polymer gels is difficult to practice where large-scale manufacturing is contemplated.

In summary, the prior art has not been able to fabricate a high-performance bipolar membrane, one 45 which possesses the desired properties listed above, which can be prepared by a straightforward and reliable procedure.

Summary of the Invention

According to the present invention there is provided a laminate structure useful in the manufacture of 45 bipolar membranes characterised in that it comprises:

1. an anionic or a cationic ion-exchange layer;
2. a non-ionic layer containing chemically reactive sites which, when reacted, will form an ion-exchange 50 layer having a charge opposite to the ion-exchange layer 1;
3. an intermediate layer interposed between said layers 1 and 2 and having ion-exchange domains of the same charge as layer 1 and reactive sites which, when reacted, will form ion-exchange domains having the same charge as layer 2.

It has been discovered that the aforesaid problems encountered in the prior art for preparing bipolar 55 membranes may be overcome by forming first a bipolar membrane precursor consisting of a laminate having at least one non-ionic layer and then converting this precursor into a bipolar membrane. The membrane precursors can be readily prepared using conventional technology for the preparation of polymer films such as film-casting and lamination. The process is easily controlled, since a high degree of process variations can be tolerated. Most significantly, the membranes prepared in accordance with the invention

have good mechanical strength and satisfy the requirements of low energy consumption, high permselectivity, long-term stability and operability at high current densities without burn-out.

In brief compass, the process of the invention comprises forming as the first layer an ion-exchange layer consisting either of an ion-exchange resin embedded in a polymeric matrix (a heterogeneous ion-exchange layer) or of a crosslinked polymer gel or entangled polymer blends containing ion-exchange groups (a homogeneous ion exchange layer). For this first layer, substantially any organic or inorganic layer or resin with ion-exchange capacity may be used. A second layer, which also may be organic or inorganic, but which has no ion-exchange capacity (the non-ionic layer), is then bonded or joined to the ion-exchange layer. The resulting composite film formed from such ion-exchange and non-ionic layers is not, in and of itself, a bipolar membrane, but rather merely a precursor of such a membrane.

It is an essential feature of the invention that the non-ionic layer be chemically reactive and have the potential to be later converted to an ion-exchange layer by treatment with suitable chemical reagents. The bonding or joining of the two layers may be accomplished by any conventional means, such as fusion through heat and pressure, solution, adhesives, or solution-casting of one layer upon the other.

After its formation, the precursor is contacted with suitable reagents which react with the chemically reactive non-ionic layer(s) to form eventually layer(s) containing ion-exchange groups or capacities.

A further modification of the process of the present invention consists of forming first a multilayer laminate having all neutral layers and then converting the layers on one side of the laminate into either cation or anion-exchange layer(s). The resulting composite then becomes the bipolar membrane precursor as described above.

In accordance with the instant invention a bipolar membrane is prepared which contains at least one interfacial layer between the anion-transfer layer and the cation transfer layer. The interfacial layer contains ion-exchange resin dispersed in a homogeneous, fixed polymer matrix having ionic groups of a charge opposite to that of the ion-exchange resin.

The membranes of this invention, surprisingly, exhibit improved performance over those membranes of the prior art in which such interfacial layer is absent.

Brief Description of the Figures

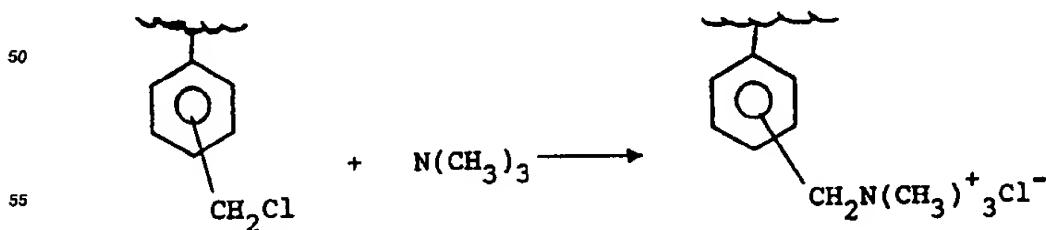
30 Figure 1 illustrates a bipolar membrane precursor made by the process of the invention.

Figure 2 shows a bipolar membrane precursor of the invention containing a reactive and a non-reactive cation exchange layer having both anionic and cationic domains.

Figure 3 depicts the bipolar membrane of the invention containing an interfacial layer having both anionic and cationic domains.

Detailed Description of the Invention

The advantages of the invention may be achieved most simply by forming a composite film containing one non-ionic layer and one ionic layer. For example, a bipolar membrane precursor can be formed by first casting a film from a mixture of a polymer such as polyvinyl chloride with crosslinked divinylbenzene (DVB) - vinyl-benzyl chloride (VBC) resin in a suitable solvent such as dimethyl-formamide (DMF) on a glass plate and evaporating the solvent in an oven. A thin coating of a DMF solution of a cation-exchange resin in a matrix polymer such as polyvinyl chloride can then be applied. The bipolar membrane precursor which results following drying is then treated with a amine, such as trimethylamine, which reacts with the benzyl chloride groups in the first layer to form anion-exchange groups as follows:



Alternatively, crosslinked polystyrene can be used as the non-ionic layer in the precursor. A polyvinylbenzyl chloride crosslinked by polyamines or diamines acting as the anion-exchange layer may then be cast upon the polystyrene. The precursor can then be sulfonated by well-known procedures. See Friedrich Helferrich, *Ion Exchange* (McGraw-Hill, New York, 1962) for a description of sulfonation procedures.

5 In order to improve the membrane performance (particularly its permselectivity) and its mechanical strength, it is often desirable to form a multilayered structure. Such a structure is depicted in Figure 1. For example, following the casting of the low resin content neutral layer (N-2) of divinylbenzene-vinylbenzyl chloride resin in polyvinyl chloride, a coating of a second high resin content neutral layer (N-1) containing the same resin in a vinylbenzyl chloride-styrene copolymer may be applied, followed by a high resin layer 10 (C-1) of cation-exchange resin in a vinylbenzyl chloride-styrene copolymer. After these, the low resin layer (C-2) of cation-exchange resin in polyvinyl chloride is cast. This membrane precursor may then be converted to bipolar membranes by amination. Layers N-1 and N-2 are converted to anion exchange layers and a bipolar membrane is formed. The resulting membrane has lower potential drops, as compared to the membranes without the additional coatings N-1 and C-1. The membranes may also be cast onto some 15 reinforcing fabrics such as polypropylene cloth or scrims for improved strength.

An embodiment of the subject invention is bipolar membranes containing an interfacial layer between the anion exchange layer and the cation exchange layer and membrane precursors therefor. The interfacial layer contains intermingled anion transfer domains and cation exchange resins. Such membranes are effective and have a particularly low potential drop.

20 The efficacy of the foregoing membranes is particularly surprising because prior to the invention it was believed that, to obtain low potential drop, significant interpenetration of the oppositely charged ion-exchange groups had to be avoided. See U.S. Patent 4,116,889, column 4.

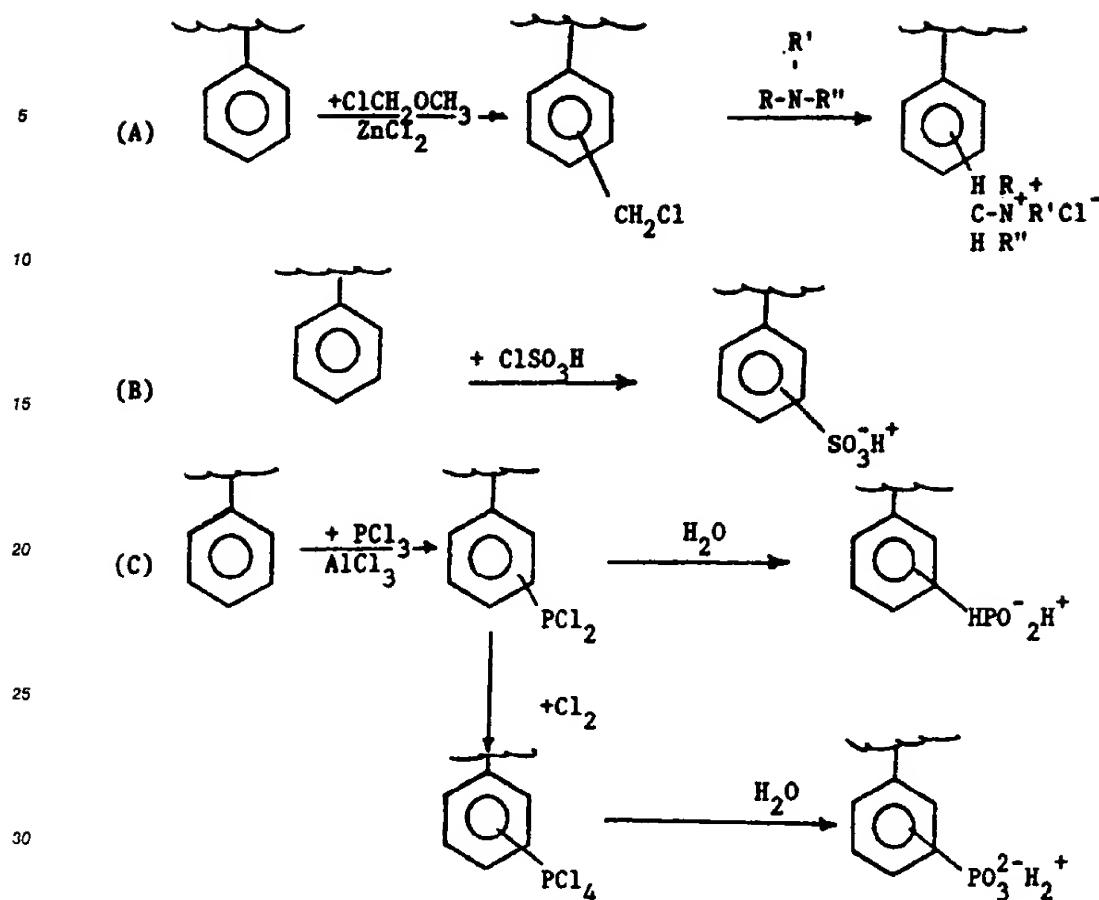
Figure 2 illustrates the membrane precursor in accordance with this embodiment of the invention. In this case, a neutral layer N-1 containing a polymer or copolymer of vinylbenzyl chloride is cast and dried. 25 Thereafter, a C-1 layer containing a cation-exchange resin and a matrix having functional groups which can be converted to anion exchange domains is formed on the N-1 layer. After drying, the final C-2 layer is cast. The latter layer, in contrast to the C-1 layer, is non-reactive, i.e., is substantially inert to the reagent used to form the anion exchange layers. Accordingly, after amination the bipolar membrane depicted in Figure 3 is formed. The previously neutral layer (N-1 in Figure 2) becomes the anion-exchange A-1 layer, and the 30 reactive C-1 layer of Figure 2 becomes the interfacial layer of Figure 3. Examples of a non-reactive C-2 layer would include those containing PVC or PVC-olefin copolymer matrices. An example of a reactive C-1 layer would be one containing a vinylbenzyl chloride-styrene copolymer matrix.

As examples of non-ionic layers, one may use divinylbenzene-vinylbenzyl chloride resin particles embedded in a polymer matrix such as polyvinyl chloride, polyvinylidene fluoride, nylon, polysulfone, 35 polystyrene; a polymer film such as polyethylene, polypropylene or polytetrafluoroethylene impregnated with divinyl benzene and styrene or vinylbenzyl chloride which are then polymerized; a polymer film or screen or scrim imbibed with styrene which is then polymerised and crosslinked by radiation such as gamma rays or electron beam; a polystyrene film crosslinked by the aforesaid radiation; and a layer of polymer or copolymer of vinylbenzyl chloride.

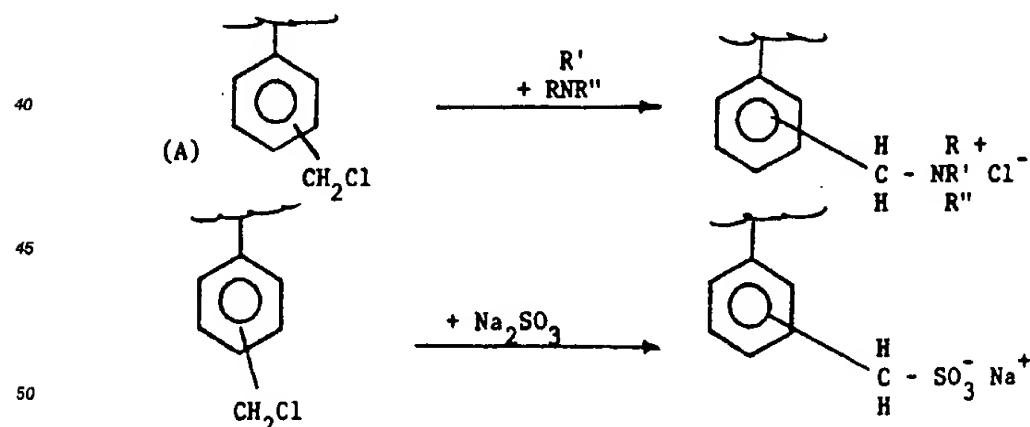
40 Various other ion-exchange layers can also be used. As examples, one may use a layer of polymer such as polyvinylchloride or polyvinylidene fluoride containing ion-exchange resin particles, such as divinylbenzene-styrene latices prepared by emulsion copolymerization and then sulfonated or divinylbenzene-vinylbenzyl chloride latices prepared by emulsion polymerization and then aminated. Alternatively one may also use a sulfonated crosslinked polystyrene sheet; a layer formed by mixing and 45 reacting a polymer or copolymers of vinylbenzyl chloride with polyamines such as tetraethylenepentamine or with diamines such as N,N-dimethyl-1, 3-propanediamine or others given below; or a layer formed by mixing and reacting formaldehyde with polyamines or diamines such as those given below.

Examples of ion-exchange groups which may be introduced into the non-ionic polymers are as follows:

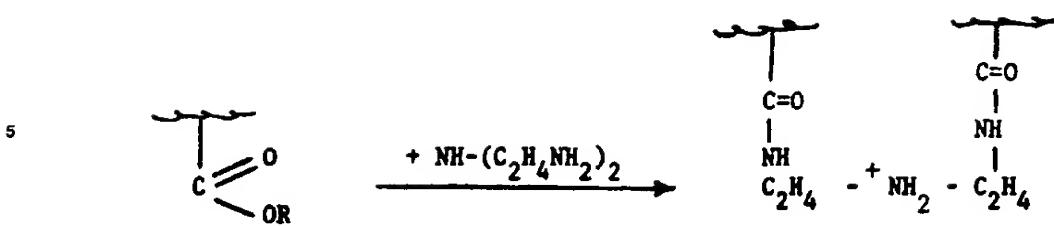
(i) Non-ionic polymers containing polymerized styrene --



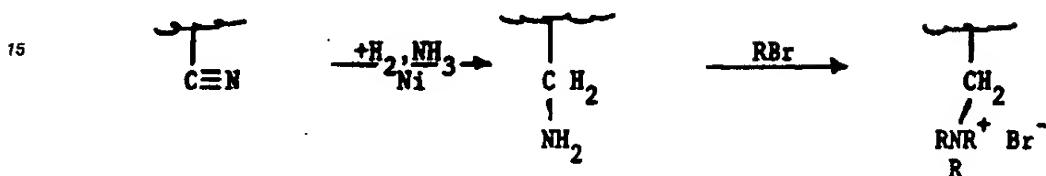
35 (ii) Non-ionic polymers containing polymerized vinylbenzyl chloride --



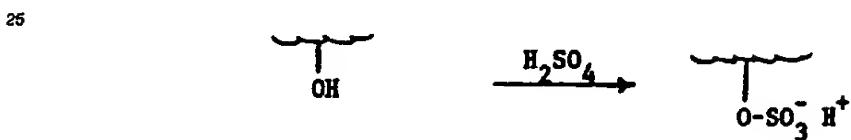
(iii) Non-ionic polymers containing polymerized acrylates --



(iv) Non-ionic polymers containing polymerized acrylonitrile --



(v) Non-ionic polymers containing polymerized vinyl alcohol --



Examples of amines useful in some of the transformations described above are: tertiary amines such as trimethylamine, triethylamine or dimethylethanolamine, secondary amines such as N-methylpropylamine, primary amines such as n-propylamine or n-butylamine, diamines such as N,N-dimethyl-1,3-propanediamine, N,N,N',N'-tetramethylxylenediamine, N,N-dimethylbutanediamine, N,N,N',N'-tetramethyl-1,6-hexanediamine, or N-methylpiperazine, and polyamines such as diethylenetriamine or tetraethylene pentamine. The symbols R, R' and R" are used to indicate organic radicals such as lower alkyl groups, e.g., CH3-, C2H5.

The following Examples I to V illustrate the process of the present invention. Examples I to V also describe novel bipolar membranes with the unique interfacial layer and their precursors.

Preparation of Polymers

A. Cation Exchange Resin (Resin A)

45 Four hundred ml of distilled water was boiled in a 1 liter three-neck distillation flask under a nitrogen gas sweep. It was then cooled to room temperature, and 6 g. of sodium lauryl sulfate was added and stirred into a solution. A mixture of 70 g. styrene and 40 g. of 55% commercial divinylbenzene was added, followed by 1 g. of K2S2O8. The reaction mixture was then heated to 60 °C and held at this temperature for 50 3 hours. Following polymerization the resin was coagulated in 10% sodium chloride solution, filtered, washed with distilled water, washed with methanol, and dried.

55 Twenty g. of the dried resin was dispersed in 200 cc. dichloroethane and added slowly to a mixture of 120 ml dichloroethane and 80 ml chlorosulfonic acid with vigorous agitation. The sulfonation reaction was allowed to proceed for 1 hour, after which the reaction mixture was poured into 1 liter of crushed ice, stirred and filtered. The slimy filter cake was then suspended in distilled water and boiled to drive off the dichloroethane. The resin, after having been filtered, resuspended in distilled water, and refiltered, was dried and redispersed in N,N-dimethylformamide (DMF). This resin was used as the cation-exchange resin for the following Examples.

B. Crosslinked Divinylbenzene-Vinylbenzyl Chloride Resin (Resin B)

Four hundred ml. of distilled water was boiled in a 1 liter three-neck flask under nitrogen. It was then cooled to room temperature and 6 g. of sodium lauryl sulfate was stirred in, followed by a mixture of 65 g. 5 vinylbenzyl chloride and 35 g. of a 77.9% commercial divinylbenzene, and then 1 g. $K_2S_2O_8$. The reaction mixture was heated to 60°C and held at this temperature for 3 hours. The resin thus prepared by emulsion polymerization was coagulated in 10% sodium chloride solution, filtered, and washed with distilled water and then with methanol. Following washing, the resin was dried in a forced-convection oven at room temperature. The dry resin was dispersed in DMF for use in membrane preparation.

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C. Vinylbenzyl Chloride-Styrene Copolymer (Resin C).

Four hundred ml distilled water was boiled in a 1 liter three-neck flask under nitrogen gas and then cooled to room temperature. Six g. of sodium lauryl sulfate was added and stirred to form a solution. The 15 solution was further cooled to 15°C, and a mixture of 39 g. vinylbenzyl chloride and 61 g. styrene was added with vigorous agitation, followed by 1 g. of $K_2S_2O_8$ and 1 g. of $Na_2S_2O_5$. The mixture was heated slowly to 35°C and held at this temperature overnight. The resultant copolymer latex was coagulated in 10% NaCl solution, filtered, and washed with distilled water and then with methanol. The wet copolymer was 20 then dried at room temperature in a forced-convection oven. A solution of the vinylbenzyl chloride-styrene copolymer in DMF was then prepared for membrane casting.

D. Crosslinked Divinylbenzene-Vinylbenzyl Chloride Resin (Resin D).

This resin was prepared following essentially the same procedure as Resin B above, except that a 25 mixture of 90 g. vinylbenzyl chloride and 10 g. of 55% commercial divinylbenzene was used instead of the monomer mixture described therein and polymerization was conducted at 70°C for 1 hour and 30 min.

Example I

30 A 0.03 cm (15 mil) thick layer of a mixture of 6% w/w of polyvinyl chloride (PVC) and 9% w/w of the divinylbenzene-vinylbenzyl chloride Resin B in DMF was cast on a glass plate by means of a doctor blade and dried in a forced-convection oven at 125°C for 12 minutes. The film was removed from the oven and a mixture of 3.75% w/w PVC and 11.25% w/w of the divinylbenzene-vinylbenzyl chloride Resin B in DMF was 35 coated on the first film. After drying in the oven for 3 minutes, the film was coated again with a mixture of 6% w/w PVC and 6% w/w of cation-exchange resin in DMF. After drying for an additional 3 minutes at 125°C, the plate was removed from the oven and a mixture of 7.4% w/w PVC and 2.6% w/w of cation-exchange Resin A in DMF was cast by means of a doctor blade to a thickness of 0.055 cm (22 mil) above the glass plate. The composite was further dried in the oven for 6 minutes, removed, cooled to room temperature, and soaked free of the glass plate in water.

40 The membrane thus prepared was then immersed in a 24% aqueous solution of trimethylamine. Following amination for about 7 days, the membrane was removed and washed free of the amine. A mechanically strong membrane was obtained. It was then tested in a test cell with a pair of Luggin tips (agar gel saturated with KCl) situated across the membrane to measure potential drops. With 1 N Na_2SO_4 solution circulating in the cell and under a current density of 1111 Am^{-2} (100 amp/ft²), the potential drop 45 across the membrane (after the proper correction of the voltage contribution from the solution) was determined to be about 1.8 volts. Furthermore, acid and base were produced during the passage of electric current through the membrane, evidencing that the membrane is indeed bipolar.

Example II

50 A 0.03 cm (15 mil) thick layer of a mixture of 5% w/w PVC in DMF and 10% w/w of the divinylbenzene-vinylbenzyl chloride Resin D was cast onto a glass plate by means of a doctor blade. The cast film was dried in a forced-convection oven at 125°C for 12 minutes. After the film was removed from the oven, a mixture of 3.75% w/w of vinylbenzyl chloride-styrene copolymer (Resin C) and 11.25% of the divinylbenzene-vinylbenzyl chloride Resin D in DMF was coated on the film. After drying in the oven at 125°C for 3 minutes, the film was coated with a mixture of 6% w/w of the copolymer and 6% w/w cation-exchange resin in DMF. Upon further drying at 125°C for 3 minutes, the plate was removed from the oven and a layer of a mixture of 7.4% w/w PVC and 2.6% w/w cation-exchange Resin A in DMF was cast thereon by means

of a doctor blade to a total thickness of 0.055 cm (22 mil) for the combined layers. The composite was dried further in the oven for 6 minutes, removed, cooled, and soaked free of the glass plate in water.

After the bipolar membrane precursor thus prepared was rinsed further with distilled water it was immersed in a mixture of 100 ml distilled water and 50 ml acetone. The membrane was allowed to swell for about 15 minutes. Five g. of a mixture of N,N-dimethyl-1,3-propanediamine (DMPDA) and N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA) in a molar ratio of 1:1 was then added to the acetone solution, and amination was allowed to proceed for 1 day. After amination, the membrane was rinsed thoroughly with distilled water. A mechanically strong membrane was obtained and its potential drop was determined to be about 1.2 volts at 1111 A. m⁻² (100 amp/ft²) when measured in 1 N Na₂SO₄ solution. Acid and base were produced during the operation.

Example III

A 0.03 cm (15 mil) thick layer of a mixture of 5% w/w PVC and 10% w/w of the divinylbenzene-vinylbenzyl chloride Resin D in DMF was cast onto a glass plate by means of a doctor blade. The cast film was dried in a forced-convection oven at 125 °C for 12 minutes. After the film was removed from the oven, a mixture of 3.75% w/w of the vinylbenzyl chloride-styrene copolymer (Resin C) and 11.25% w/w of the divinylbenzene-vinylbenzyl chloride Resin D in DMF was coated on the film. After drying in the oven at 125 °C for 3 minutes, the first film was coated again with a mixture of 6% w/w of the copolymer and 6% w/w cation-exchange Resin A in DMF. After drying in the oven at 125 °C for an additional 3 minutes, the plate was removed and a mixture of 7.4% w/w PVC and 2.6% w/w cation-exchange Resin A in DMF was cast by means of a doctor blade to a thickness of 0.055 cm (22 mil) for the combined layers. The whole film composite was dried further in the oven for 6 minutes, removed, cooled, and soaked free of the glass plate in water.

The membrane thus prepared was rinsed further with distilled water and immersed in a mixture of 100 ml. water and 50 ml. acetone. The membrane was allowed to swell for about 15 minutes. Five g. of a mixture of DMPDA and TMHDA in a molar ratio of 3:1 was then added to the acetone solution, and amination was allowed to proceed for one day. After amination, the membrane was rinsed thoroughly with distilled water. A mechanically strong membrane was obtained. It was then placed in the test cell for determination of its water-splitting potential. In 1 N Na₂SO₄ solution the potential drop across the membrane was about 1.2 volts at a current density of 1111 Am⁻² (100 amp/ft²). Acid and base were produced during the operation.

Example IV

A 0.03 cm (15 mil) thick layer of a mixture of 5% w/w PVC and 10% w/w of the divinylbenzene-vinylbenzyl chloride Resin D was cast onto a glass plate by means of a doctor blade. The cast film was dried in a forced-convection oven at 125 °C for 12 minutes. The film was removed from the oven and a mixture of 3.75% w/w PVC and 11.25% w/w of the divinylbenzene-vinylbenzyl chloride Resin D was coated on the film. After drying in the oven at 125 °C for 3 minutes the film was coated with a mixture of 6% w/w PVC and 6% w/w cation-exchange Resin A in DMF. After drying in the oven at 125 °C for an additional 3 minutes, the plate was removed and a mixture of 7.4% w/w PVC and 2.6% w/w cation-exchange Resin A in DMF was cast by means of a doctor blade to a thickness of 0.055 cm (22 mil) for the combined layers. The composite was dried further in the oven for 6 minutes, removed, cooled, and soaked free of the glass plate in water.

The membrane thus prepared was aminated as described in Example III. The resulting bipolar membrane had a potential drop of about 2.0 volts at a current density of 1111 Am⁻² (100 amp/ft²), when measured in 1 N Na₂SO₄ solution. Acid and base were produced during the operation.

Example V

A 0.03 cm (15 mil) thick layer of a mixture of 6% w/w PVC and 9% w/w of the divinylbenzene-vinylbenzyl chloride Resin D (with 5.5% DVB) in DMF was cast onto a glass plate by means of a doctor blade. The cast film was then dried in a forced-convection oven at 125 °C for 12 minutes. After the film was removed from the oven, a mixture of 3.75% w/w PVC and 11.25% w/w of the divinylbenzene-vinylbenzyl chloride Resin D was coated on the first film. After drying in the oven at 125 °C for 3 minutes, the film was coated again with a mixture of 6% w/w of the vinylbenzyl chloride-styrene copolymer (Resin C) and 6% w/w cation-exchange Resin A in DMF. After drying in the oven at 125 °C for an additional 3 minutes, the plate

was removed and a mixture of 7.4% w/w PVC and 2.6% w/w cation-exchange Resin A in DMF was cast by means of a doctor blade to a thickness of 0.055 cm (22 mil) for the combined layers. The composite was dried further in the oven for 6 minutes, removed, cooled, and soaked free of the glass plate in water.

After the membrane thus prepared was rinsed further with distilled water, it was immersed in a mixture of 100 ml. water and 50 ml. acetone. The membrane was allowed to swell for about 15 minutes. Five g. of a mixture of DMPDA and TMHDA in a molar ratio of 1:1 was then added to the acetone solution, and amination was allowed to proceed for one day. Following amination, the membrane was rinsed thoroughly with distilled water. A mechanically strong membrane was obtained. It was then placed in a test cell for determination of its water-splitting potential. In 1 N Na_2SO_4 solution the potential drop across the membrane was about 1.3 volts at a current density of 1111 Am^{-2} (100 amp/ ft^2). Acid and base were produced during the operation.

Comparative Example

To demonstrate that the novel procedure for preparing bipolar membranes of the invention gives membranes which are different from those prepared by the conventional procedure, i.e., where the anion-exchange resin in the anion-transfer layers is aminated before membrane casting, the following example is given:

An anion-exchange resin was prepared as follows: Five g. of the divinylbenzene-vinylbenzyl chloride Resin D was dispersed in 50 cc. acetone and stirred for several hours. Seven g. of a mixture of DMPDA and TMHDA in a molar ratio of 1:1 was added. Amination proceeded for about 2 days and the resin was then filtered, washed with distilled water, and dried at room temperature.

A 0.03 cm (15 mil) thick layer of a mixture of 6% w/w PVC and 9% w/w of the anion-exchange resin in DMF was cast onto a glass plate by means of a doctor blade. The cast film was then dried in a forced-convection oven at 125°C for 12 minutes. The film was removed from the oven and a mixture of 3.75% w/w PVC and 11.25% w/w of the anion-exchange resin was coated on the film. After drying in the oven at 125°C for 3 minutes, the film was coated with a mixture of 6% w/w of the vinylbenzyl chloride-styrene copolymer (Resin C) and 6% w/w cation-exchange Resin A in DMF. Upon further drying in the oven at 125°C for an additional 3 minutes, the plate was removed and a mixture of 7.4% w/w PVC and 2.6% w/w cation-exchange Resin A in DMF was cast by means of a doctor blade to a thickness of 0.055 cm (22 mil) for the combined layers. The composite was dried further in the oven for 6 minutes, removed, cooled, and soaked free of the glass plate in water.

The potential drop across the membrane was then measured in the test cell with 1 N Na_2SO_4 solution circulating. At a current density of 1111 Am^{-2} (100 amp/ ft^2), membrane voltage was about 1.8 volts. Acid and base were produced during the operation.

Comparing the above with Example V, it can be seen that the bipolar membrane prepared by the process of the invention has a lower voltage, 1.3 volts versus 1.6 volts. Therefore the bipolar membrane of the invention is different from and, indeed, superior to the membrane prepared by the conventional procedure.

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Claims

1. A laminate structure useful in the manufacture of bipolar membranes characterised in that it comprises:
 - (1) an anionic or a cationic ion-exchange layer;
 - (2) a non-ionic layer containing chemically reactive sites which, when reacted, will form an ion-exchange layer having a charge opposite to the ion-exchange layer 1;
 - (3) an intermediate layer interposed between said layers 1 and 2 and having ion-exchange domains of the same charge as layer 1 and chemically reactive sites which, when reacted, will form ion-exchange domains having the same charge as layer 2.
2. A laminate structure according to claim 1, characterised in that layer 1 is substantially free of such reactive sites.
3. A laminate structure according to claim 1 or claim 2 characterised in that the non-ionic layer consists of divinylbenzene-vinylbenzyl chloride resin in a matrix polymer and the ion-exchange resin layer consists of cation-exchange resin in a matrix polymer.
4. A bipolar membrane structure characterised in that it comprises anionic and cationic layers and at least

one interfacial layer as defined in claim 1 composed of an ion-exchange resin dispersed in a homogeneous, fixed polymer matrix having ionic groups, such that the matrix and the resin are oppositely charged.

5. A structure according to claim 4 characterised in that the resin is a cation-exchange resin, and the matrix is vinylbenzyl chloride-styrene copolymer aminated and crosslinked by diamines or polyamines, or mixed amines.
10. 6. A process for preparing a bipolar membrane characterised in that it comprises intimately contacting a laminate composed of:
 - (1) an anionic or cationic ion-exchange layer;
 - (2) a non-ionic layer containing chemically reactive sites; and
 - (3) an intermediate layer interposed between said layers 1 and 2 and having ion-exchange domains of the same charge as layer 1 and chemically reactive sites;
15. with a reagent which converts the reactive sites in both layers 2 and 3 to ionic groups which have a charge opposite to the charge on said ion-exchange layer 1.
7. A process according to claim 6 characterised in that said non-ionic layer is aminated to form an anion-exchange layer, and the ion-exchange layer is a cation-exchange resin in a polymer matrix.
20. 8. A process according to claim 6 characterised in that the non-ionic layer is aminated with an organic amine having from 1 to 1000 carbon atoms.
9. A process according to claim 8 characterised in that the amine contains at least two primary, secondary, or tertiary amine groups.
25. 10. A process according to claim 7 characterised in that the amine is at least one of the compounds selected from N,N-dimethyl-1,3-propanediamine and N,N,N',N'-tetramethyl-1,6-hexanediamine.
30. 11. A process according to claim 6 characterised in that the non-ionic layer is sulfonated to form a cation-exchange layer and the ion-exchange layer is an anion-exchange layer.
12. A process according to claim 6 characterised in that the non-ionic layers consist of a layer of divinylbenzene-vinylbenzyl chloride resin in an inert polymer matrix joined to a layer of the same resin in a polymer matrix, and the ionic layers consist of a layer containing cation-exchange resin in a vinylbenzyl chloride-styrene copolymer joined to the non-ionic layers, and an additional layer containing cation-exchange resin in an inert polymer matrix.
35. 13. A process according to claim 6 characterised in that it comprises forming a first layer containing PVC and a divinyl-benzene-vinylbenzyl chloride resin; drying said layer; forming upon said first layer a second layer having the same polymeric constituents as the first layer but with a lesser amount of polyvinyl chloride; drying said second layer; forming a third layer on said second layer, said layer containing a vinyl benzyl chloride-styrene co-polymer and a cation-exchange resin; drying said third layer; forming on said third layer a fourth layer containing polyvinyl-chloride and a cation-exchange resin; drying said fourth layer; and thereafter aminating the resulting structure so as to convert said first and second layers to anion-exchange layers.

Revendications

50. 1. Structure stratifiée utilisable pour la fabrication de membranes bi-polaires caractérisée en ce qu'elle comporte:
 - (1) une couche d'échange d'ions anioniques ou cationiques
 - (2) une couche non ionique comportant des sites chimiquement réactifs lesquels, lorsqu'ils ont réagi, formeront une couche d'échange d'ions ayant une charge opposée à celle de la couche d'échange d'ions (1)
 - (3) une couche intermédiaire insérée entre les deux dites couches (1) et (2) et ayant des zones d'échange d'ions de la même charge que la couche (1) et des sites chimiquement réactifs lesquels, lorsqu'ils ont réagi, formeront des domaines d'échange d'ions ayant la même charge

que la couche (2).

2. Structure stratifiée selon la revendication 1, caractérisée en ce que la couche (1) est sensiblement libre de tels sites réactifs.
- 5 3. Structure stratifiée selon la revendication 1 ou 2, caractérisée en ce que la couche non ionique est constituée d'une résine de chlorure de divinyl benzène-vinylobenzyle dans une matrice polymérique et la couche de résine échangeuse d'ions est constituée d'une résine échangeuse d'ions dans une matrice polymérique.
- 10 4. Structure de membrane bi-polaire caractérisée en ce qu'elle comprend des couches anioniques et cationiques et au moins une couche intermédiaire telle que définie dans la revendication 1 et composée d'une résine d'échange d'ions dispersée dans une matrice polymérique, fixe, homogène et ayant des groupes ioniques tels que la matrice et la résine sont de charge opposée.
- 15 5. Structure selon la revendication 4, caractérisée en ce que la résine est une résine d'échange de cation et la matrice est un copolymère de styrène et chlorure de vinyl benzyle aminé et réticulé par des diamines ou polyamines ou des mélanges d'amines.
- 20 6. Procédé pour la préparation de membranes bi-polaires, caractérisé en ce qu'il comporte la mise en contact intime d'un stratifié composé de:
 - (1) une couche d'échange d'ions anioniques ou cationiques
 - (2) une couche non ionique contenant des sites chimiquement réactifs; et
 - (3) une couche intermédiaire insérée entre lesdites couches (1) et (2) et ayant des zones d'échange d'ions de la même charge que la couche (1) et des sites chimiquement réactifs; avec un réactif qui transforme les sites réactifs dans les deux couches (2) et (3) en groupes ioniques ayant une charge opposée à la charge de ladite couche d'échange d'ions (1).
- 25 7. Procédé selon la revendication 7, caractérisé en ce que ladite couche non ionique est aminée pour former une couche d'échange d'anions et la couche d'échange d'ions est une résine échangeuse de cations dans un matrice polymérique.
- 30 8. Procédé selon la revendication 6, caractérisé en ce que la couche non ionique est aminée avec une amine organique ayant de 1 à 1000 atomes de carbone.
- 35 9. Procédé selon la revendication 8, caractérisé en ce que l'amine contient au moins deux groupes d'amines primaires, secondaires ou tertiaire.
- 40 10. Procédé selon la revendication 7, caractérisé en ce que l'amine est au moins l'un des composés sélectionnés dans le groupe comportant N, N-diméthyl-1,3-propanediamine et N,N,N',N' tétraméthyl-1,6-hexanediamine.
- 45 11. Procédé selon la revendication 6, caractérisé en ce que la couche non ionique est sulfonée pour former une couche d'échange de cations et la couche d'échange d'ions est une couche d'échange d'anions.
- 50 12. Procédé selon la revendication 6, caractérisé en ce que les couches non ioniques consistent d'une couche de résine de chlorure de divinyl benzène-vinylobenzyle dans une matrice inerte polymérique associée à une couche de la même résine dans une matrice polymérique, et les couches ioniques sont constituées d'une couche contenant une résine échangeuse de cations dans un copolymère de styrène et chlorure de vinylbenzyle associée aux couches non ioniques et une couche additionnelle contenant une résine échangeuse de cations dans une matrice polymérique inerte.
- 55 13. Procédé selon la revendication 6, caractérisé en ce qu'il comprend les étapes de formation d'une première couche contenant du PVC et une résine de chlorure de divinyl benzène-vinylobenzyle, le séchage de cette couche, la formation sur ladite première couche d'une seconde couche ayant les mêmes éléments constituants polymériques que la première couche mais avec un montant plus faible de chlorure de polyvinyle, le séchage de ladite seconde couche, la formation d'une troisième couche sur ladite seconde couche, ladite couche contenant un copolymère de styrène et de chorure de vinyl-

benzyle résine échangeuse de cations, le séchage de ladite troisième couche, la formation sur ladite troisième couche d'une quatrième couche contenant un chlorure de polyvinyle et une résine échangeuse de cations, le séchage de ladite quatrième couche ; ensuite de quoi on amine la structure résultante de façon à convertir lesdites première et seconde couche en couche échangeuse d'anions.

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Patentansprüche

1. Laminat-Struktur, insbesondere zur Herstellung bipolarer Membranen, gekennzeichnet durch
 - (1) eine anionische oder kationische Ionen austausch-Schicht,
 - (2) eine nicht-ionische Schicht mit chemisch reagierenden Stellen, die bei Reaktion eine Ionen-Austausch-Schicht mit einer Ladung entgegen der Ionen-Austausch-Schicht 1 bildet,
 - (3) eine Zwischenschicht zwischen den Schichten 1 und 2 mit Ionen-Austausch-Bereichen der gleichen Ladung wie Schicht 1 und mit chemisch reagierenden Stellen, die bei Reaktion Ionen-Austausch-Bereiche mit der gleichen Ladung wie Schicht 2 bilden.
- 15 2. Laminat-Struktur nach Anspruch 1, dadurch gekennzeichnet, daß die Schicht 1 im wesentlichen frei ist von derart reagierenden Stellen.
3. Laminat-Struktur nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die nicht-ionische Schicht aus Divinylbenzol-Vinylbenzylchlorid-Harz in einem Matrix-Polymer und die Ionen-Austausch-Harzschicht aus Kationenaustausch-Harz in einem Matrix-Polymer besteht.
- 20 4. Bipolare Membran-Struktur dadurch gekennzeichnet, daß diese anionische und kationische Schichten und wenigstens eine Grenzflächenschicht nach Anspruch 1 enthält, die aus einem Ionen-Austausch-Harz besteht, das in einer homogenen festen Polymer-Matrix mit Ionengruppen in der Weise dispergiert ist, daß die Matrix und das Harz gegensätzlich geladen sind.
- 25 5. Struktur nach Anspruch 4, dadurch gekennzeichnet, daß das Harz ein Kationen-Austausch-Harz ist und die Matrix ein Vinylbenzyl Chloride-Styrol Copolymer ist, das aminiert und durch Diamine oder Polyamine oder gemischte Amine vernetzt ist.
- 30 6. Verfahren zur Herstellung einer bipolaren Membran, dadurch gekennzeichnet, daß ein Laminat mit
 - (1) einer anionischen oder kationischen Ionen-Austausch-Schicht
 - (2) einer nicht-ionischen Schicht, die chemisch reagierende Stellen aufweist, und
 - (3) einer Zwischenschicht, die zwischen den Schichten 1 und 2 liegt und Ionen-Austausch-Bereiche der gleichen Ladung wie Schicht 1 und chemisch reagierende Stellen aufweist,
mit einem Reagenz innig kontaktiert wird, das die reagierenden Stellen der beiden Schichten 2 und 3 in Ionengruppen wandelt, die eine gegensätzliche Ladung gegenüber der Ladung der Ionen-Austausch-Schicht 1 aufweisen.
- 35 7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die nicht-ionische Schicht zur Bildung einer Anionen-Austausch-Schicht aminiert ist und die Ionen-Austausch-Schicht ein Kationen-Austausch-Harz in einer Polymer-Matrix ist.
- 40 8. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die nicht-ionische Schicht mit einem organischen Amin aminiert ist, das 1 bis 100 Kohlenstoffatome enthält.
- 45 9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das Amin wenigstens zwei primäre, sekundäre oder tertiäre Amin-Gruppen enthält.
- 50 10. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Amin wenigstens aus einer der Verbindungen N,N-Dimethyl-1,3-propan diamin und N,N,N',N'-Tetramethyl-1,6-hexandiamin ausgewählt ist.
- 55 11. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die nicht-ionische Schicht sulfoniert ist, um eine Kationen-Austausch-Schicht zu bilden und die Ionen-Austausch-Schicht eine Anionen-Austausch-Schicht ist.

12. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die nicht-ionischen Schichten aus einer Schicht aus Divinylbenzol-Vinylbenzylchlorid-Harz in einer inerten Polymer-Matrix bestehen, die mit einer Schicht des gleichen Harzes in einer Polymer-Matrix gebunden sind, und die Ionen-Schichten aus einer Schicht mit Kationen-Austausch-Harz in einem Vinylbenzolchlorid-Styrol Copolymer, das mit den nicht-ionischen Schichten verbunden ist, und einer zusätzlichen Schicht, die Kationen-Austausch-Harz in einer inerten Polymer-Matrix enthält, bestehen.

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13. Verfahren nach Anspruch 6, gekennzeichnet durch Bildung einer ersten Schicht aus PVC und einem Divinylbenzol-Vinylbenzylchlorid-Harz, Trocknen dieser Schicht, Bildung einer zweiten Schicht mit den gleichen Polymer Bestandteilen wie die erste Schicht, jedoch mit einer geringeren Menge an Polyvinylchlorid, Trocknen der zweiten Schicht, auf der zweiten Schicht Bildung einer dritten Schicht, die ein Vinylbenzylchlorid Styrol Copolymer und ein Kationen-Austausch-Harz enthält, Trocknen der dritten Schicht, auf der dritten Schicht Bildung einer vierten Schicht, die Polyvinylchlorid und ein Kationen-Austausch-Harz enthält, Trocknen der vierten Schicht, und anschließendes Aminieren der erhaltenen Struktur, um die ersten und zweiten Schichten in Anionen-Austausch-Schichten zu wandeln.

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